Overview of Transition Phenomenon in Nylon 6

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Introduction

Although nylons have been known since the 1930s, new transitions and/or interpretations continue to appear in the recent literature.[1-3] The purpose of this paper is to briefly summarize the known information and introduce yet another transition in nylons.

Experimental Section

Commercially available film grade nylon 6, nylon 66, and nylon 12 resins were used in this study. About 1% powder Laponite (a commercially available clay material) was added to the nylon resins, and thin filaments (0.03-in. diameter) were extruded in a capillary rheometer at a shear rate of about 100 s^{-1} at approximately 40 °C above the polymer melting temperature.

Most of the characterization was done on a Du Pont 9900 differential scanning calorimeter (DSC), and the experimental details are given in the figure captions.

Results and Discussion

First we will briefly summarize the information on nylon 6 transitions known in the literature. This will be followed by our present work leading to the identification of a new sub-T_m transition in nylons. Finally, we will comment on the anomalous doublet melting behavior of nylons when these are crystallized at moderate cooling rates.

Transitions in Nylon 6. When a nylon 6 sample is heated, several relaxations and transitions are observed over the temperature range −150 to 250 °C. Following is the discussion of these processes in the order of increasing temperature.

A γ-relaxation is observed in dynamic mechanical experiments at about −115 °C and is unaffected by moisture, crystallinity, molecular weight, etc. This is assigned to the motion of three or more CH_2 sequences.[1]

A β-relaxation is observed in dynamic mechanical experiments at about −55 °C.[1] This has been attributed to the mobility of H-bonded $>C{=}O$ groups, and its position depends upon the moisture content.[1] Starkweather[4] has proposed that water molecules interfere with the H-bonding in the nylons. Our own work has shown that a well-dried nylon 6 (e.g., 175 °C/17 h) shows a hardly detectable β-peak at about −25 °C.[5] In the presence of 1% or more moisture, the peak gains intensity and shows up at about −55 °C, presumably due to the weakened H-bonding.[4]

An α-relaxation with onset at about 45 °C (or damping maximum at about 65 °C) in dynamic mechanical analysis (DMA) is the same as T_g observed by DSC and many other techniques. The α-peak temperature is lowered by moisture, while crystallinity and orientation reduce its intensity and broaden the transition.

Sufficiently amorphous samples of nylon 6 exhibit a cold crystallization peak at about 70 °C in the DSC technique. The crystals at that temperature are primarily in the γ-crystalline form.[5]

The temperature range 80–190 °C involves a number of simultaneous processes, thus making the interpretations very difficult: (A) Depending upon the annealing temperature, T, a small endothermic peak attributed to the melting of microcrystals, is observed at about T + 20 °C in the DSC technique.[2] (B) Over this broad temperature region, the conversion of any γ-crystals to the α-form also takes place; this process is detected by X-ray diffraction (XRD), infrared (IR), and nuclear magnetic resonance (NMR) but not by DSC or DMA. (C) If the samples were not very slowly cooled or annealed, the phenomenon of crystal thickening/perfection would occur. DSC or DMA unlike XRD is not sensitive to this gradual process. (D) Recently, a Brill transition (crystal-to-crystal) has been reported in nylon 6 between 80 and 170 °C on the basis of XRD and NMR studies.[3] DSC and DMA cannot detect such a transition at least in the melt-crystallized samples. (E) Using an especially high temperature annealed (220 °C/60 h) nylon 6, an α'-relaxation at approximately 170 °C has been reported on the basis of DMA; this relaxation was associated with the mobility of interfacial amorphous phase which requires crystal mobility as a precursor.[2]

New Sub-T_m Transition in Nylons. This exothermic transition at about 195 °C in nylon 6 has long been observed by us.[5] Recently we have observed a similar sub-T_m exotherm in nylon 66 and nylon 12 (Figure 1). The sub-T_m exotherm is observed to some extent in shock-cooled nylons, but a combination of mechanical stresses and rapid cooling (e.g., in melt extrudates from a capillary rheometer) enhances the development of this transition. Moreover, the addition of non-nucleating minerals, such as Laponite and montmorillonite, further enhances the transition.

Although the sub-T_m exotherm is clearly seen in the DSC thermograms, other techniques have not been able to shed further light. For example, variable-temperature IR studies over the 175–215 °C temperature region (i.e., covering of the 195 °C transition) have not revealed any specific changes except for a slight broadening of the bands. Solid-state ^{13}C NMR indicated no dramatic changes in the T_{1c} and T_{2c} relaxation times within the sub-T_m transition zone. We would have expected major changes in the event of a phase transformation. Rather, a steady decrease in T_{1c} with increasing temperature was observed in accordance with the increased mobility but without a change in mechanism. Using XRD, samples of nylon 6 with the 195 °C transition and without the transition (e.g., by annealing at 200 °C; Figure 1) were characterized at room temperature. The crystallinity and the α:γ-crystal ratio were found to be quite similar for the two samples. The crystallite size and perfection of the α-crystals were higher for the 200 °C exposed sample, but that is to be expected. As shown in Figure 1, the sub-T_m transition is temperature specific for a particular nylon; i.e., it cannot be eliminated by annealing below it. In addition, the heating rate, e.g., 0.1–50 °C/min, does not change this transition. We must mention that a sub-T_m exotherm reported here is associated with *nylons* and we have not observed this behavior with other common semicrystalline polymers.

On the basis of the above information, we propose that the 195 °C exothermic transition is due to the release of strain energy absorbed during processing. An exotherm in the T_g region is well documented for polymers frozen under mechanical stresses.[6] These mechanical stresses are frozen-in in the form of high-energy conformations, and the strain energy is released when the polymer segments acquire mobility at a T_g. Since the sub-T_m exotherm is typically associated with the nylons,[5] it appears that H-bonding might play some role. It is possible that

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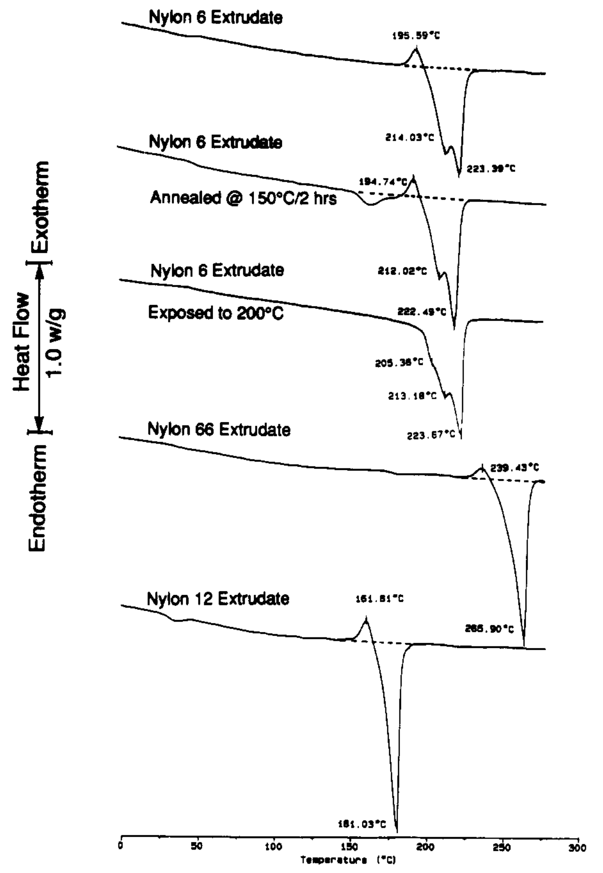

Figure 1. DSC thermograms at 10 °C/min showing the sub-T_m exothermic transition in nylon 6, nylon 66, and nylon 12 (sample size 9.0 ± 0.7 mg).

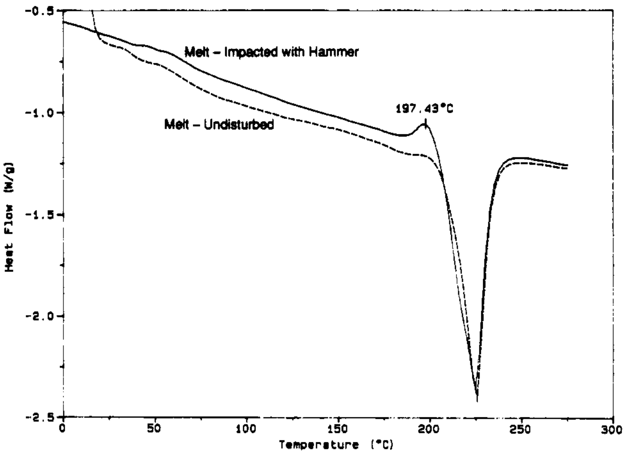

Figure 2. DSC thermograms at 10 °C/min showing the correspondence of the sub-T_m exotherm in nylon 6 to the mechanical history (sample size 9.0 ± 0.7 mg).

the thermomechanical stresses upon rapid cooling of the nylon melts get frozen-in and locked through H-bonding. Considering that such is the case, frozen-in strains might not be released at the T_g. It is possible that the strain energy is released in the sub-T_m region where the polymer segments have enhanced mobility. The correspondence of the 195 °C exotherm to the strain energy release is reinforced by the results in Figure 2. As a speculation, we can point out that the frozen-in stresses might be located in the interlamellar regions which become mobile at the pre-melt temperatures.[2] Our recent work on the process-induced memory effects in nylons is a further support to the role of H-bonding in preserving the melt history.[7]

Under similar processing history, the heats of sub-T_m exotherm for nylon 6, nylon 66, and nylon 12 are 6.3, 6.7, and 8.9 J/g, respectively. The values reported here for the sub-T_m exotherm are about the highest we have come across for these systems. These values as percentage of the heat of fusion (i.e., crystallinity measure) are 12, 13, and 19% for nylon 66, nylon 6, and nylon 12, respectively. Future work might reveal why nylon 12 is the most sensitive polymer in terms of strain energy absorption.

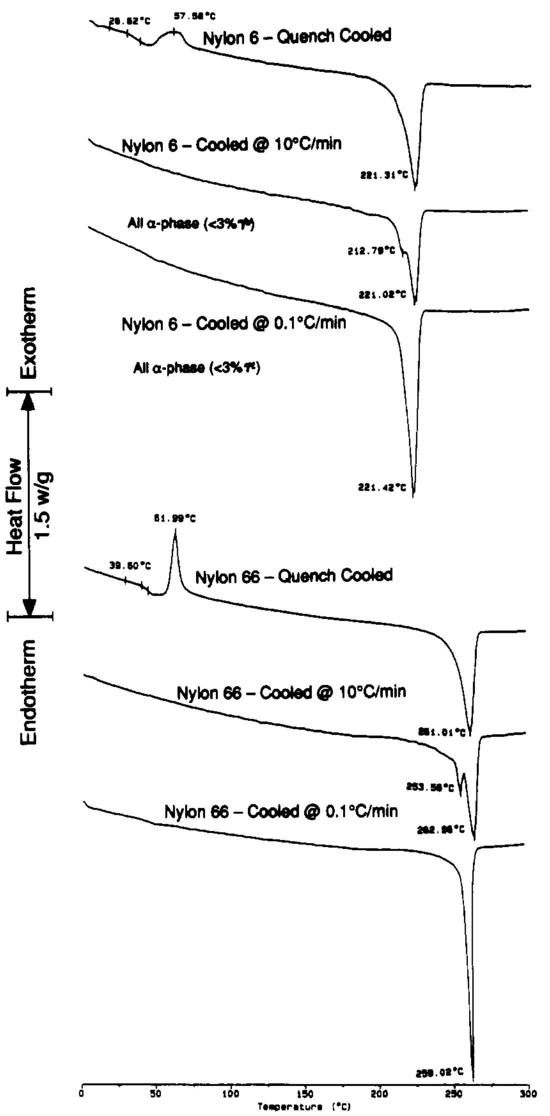

Figure 3. DSC thermograms at 10 °C/min showing the doublet melting behavior in nylon 6 and nylon 66 only when intermediate cooling rates are employed during their crystallization (sample size 1.0 ± 0.1 mg).

Doublet Melting in Nylons. Nylon 6 is known to have two crystal forms melting at 215 (γ-form) and 225 °C (α-form).[8] As a result, when one comes across a doublet melting at 215 + 225 °C, it is likely to be associated with the two crystal forms. We report that a doublet melting behavior is common to nylons including nylon 66, which melts only in one crystal form, doublet melting being a characteristic of melts crystallized at moderate cooling rates, e.g., 10 °C/min (Figure 3). Note that the crystallinities of nylon 6 or nylon 66 are very similar regardless of the cooling rate (0.1 or 10 °C/min), and the nylon 6 is predominantly in α-phase (<3% γ-phase), irrespective of the cooling rate used (Figure 3).

It appears that at high cooling rates, e.g., quenching, the imperfect crystals undergo a continuous thickening/perfection process in the T_g–T_m region and, therefore, melt at a higher temperature, e.g., 222 °C for nylon 6. At low cooling rates, e.g., 0.1 °C/min, the resulting crystals are quite perfect and, thus, melt at a higher temperature, e.g., 222 °C for nylon 6. Apparently at intermediate cooling rates, e.g., 10 °C/min, a bimodal crystallite distribution may occur and result in a doublet melting. We are aware of the multiple melting characteristics of semicrystalline polymers[9] but feel that the doublet melting observed in nylon 6 and nylon 66 at moderate cooling rates is not typically observed in other semicrystalline polymers.

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